Heterogeneous Interactions of NO_2 with Aqueous Surfaces

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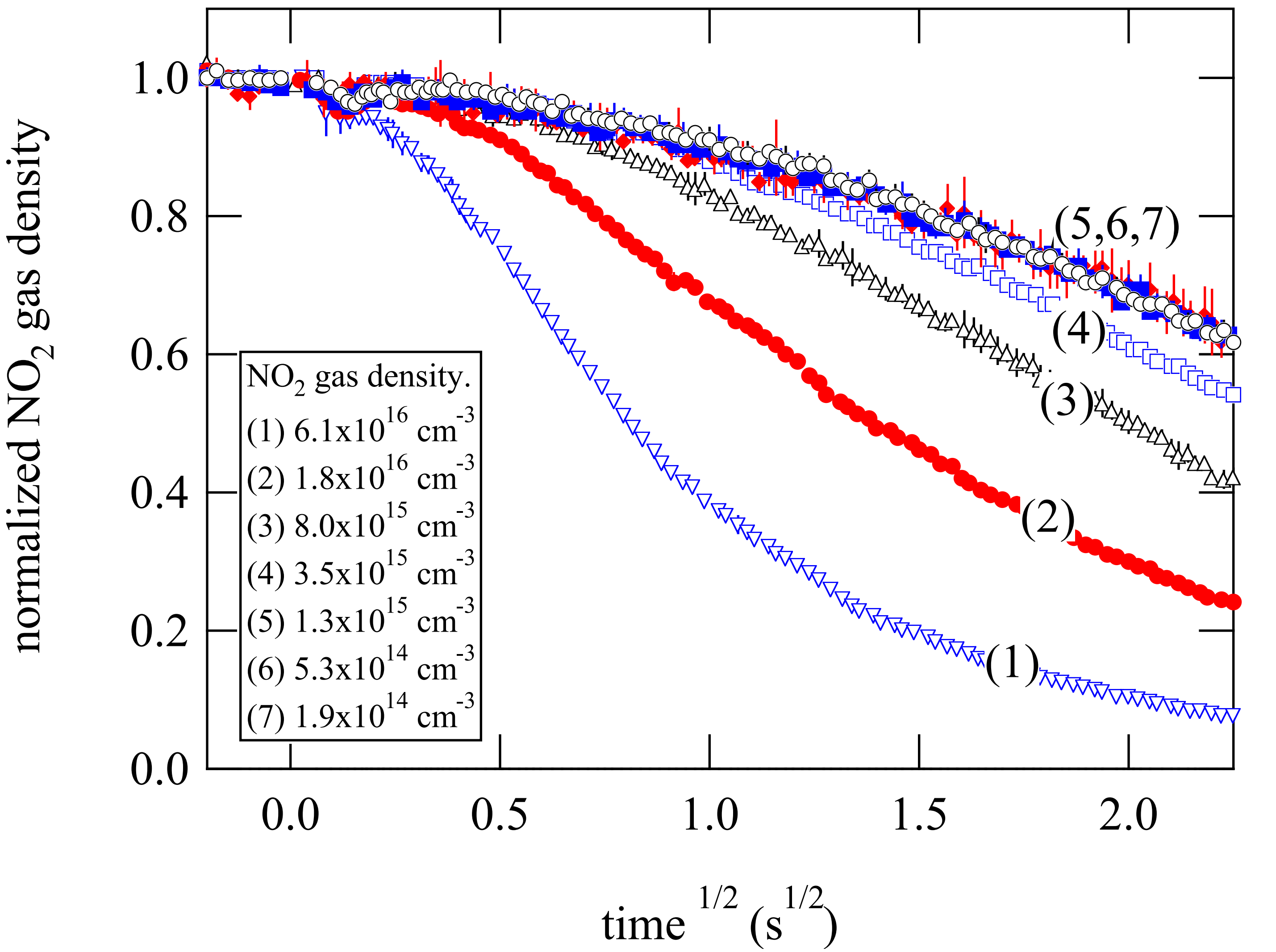
In aqueous phase, NO_2 undergoes a second order self-reaction to form HNO_2 and HNO_3. Therefore, in general, the rate of NO_2 uptake into water depends both on solubility and reactivity. As a result, except for relatively short gas-liquid interaction times, the uptake is a function of the product of the Henry's law coefficient (H) and the second order reaction rate coefficient (k_2), in the form $Hk_2^{1/2}$. In previous studies these two parameters could not be unambiguously separated and were estimated by extrapolation. Further, the estimates were made difficult by the formation, at relatively high partial pressures, of the highly soluble dimer, N_2O_4.

The uptake of NO_2 was studied in the bubble train apparatus. Here the uptake can be measured at a relatively low NO_2 density and in the range of gas-liquid interaction times 0.1s to 10s. With this apparatus it was possible to separate clearly the effects of solubility and reaction on the NO_2 gas uptake. From the measurements, H was determined to be $(1.6\pm0.2)\times10^{-2}$ M atm^{-1} and the upper limit of k_2 was set at 1.2×10^{7} M^{-1}s^{-1}.

Studies with both the droplet train and the bubble train apparatuses failed to confirm the presence of a NO_2 surface complex reported earlier by Mertes and Wahner, 1995. Our studies indicate that experimental artifacts arising from reactions on the surface of the reaction chamber can be mistaken for a surface complex.

Mertes S. and Wahner A. J. Phys. Chem. 99, p14000-14006, 1995.

Heterogeneous Uptake of NO_2 by Water Surfaces



Comparisons of Henry's Law Coefficient and Second Order Reaction Rate Constant for NO_2.

Reference	Temp (°C)	$n_g x10^{-15}$ (molec/cc)	$Hx10^2$ ($Matm^{-1}$)	$k_2 x10^{-7}$ ($M^{-1}s^{-1}$)	$Hk_2^{1/2}$ ($M^{1/2}\ atm^{-1}s^{-1/2}$)
this work	20	0.08-1.3	**1.6**	≤1.2	**55.4**
Komiyama and Inoue (1980)	15	0.3-15	2.35		
Andrew and Hanson (1961)	25	5.0-17	4.1		
Lee and Schwartz (1981)	22	0.0025-20	0.7	10	**70.0**
Cape et al.	10	$2x10^{-4}$ to $1x10^{-3}$	5.5	6.0	**134.2**
Park and Lee (1988)	22		2.0	8.4	**184.4**
Abel and H. Schmid (1928a)	25				**63.7**
Abel and H. Schmid (1928b)	25				**65.2**
G. Schmid and Bähr (1964)	25				**66.5**
Komiyama and Inoue (1978)	25				**92.9**
Komiyama and Inoue (1978)	15				**106.8**
Jordan and Bonner (1973)	25				**58.3**
Heckner (1973)	25				**113.6**
Grätzel et al (1969)	20			**6.5**	
Treinin and Haydon (1970)	25			**4.7**	
Moll (1966)	20			**2.6**	

Red bold indicates primary measurement